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PCT/GB 98/03241

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/03241

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| X | DE 196 53 196 A (MANDO MACHINERY CO) 26 June 1997 | 1,3,6,7, 10-16,19 |
| A | see example 1 | 20,21, 26-28 |
| A | US 5 262 195 A (MOSS MARY G ET AL) 16 November 1993 see the whole document | 1-32 |
| A | US 5 520 852 A (IKKALA OLLI ET AL) 28 May 1996 see the whole document | 1-32 |

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Information on patent family members

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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|---|--|
| DE 19653196 A | 26-06-1997 | CN 1158349 A JP 9183945 A | 03-09-1997 15-07-1997 |
| US 5262195 A | 16-11-1993 | NONE | |
| US 5520852 A | 28-05-1996 | AU 693558 B AU 2618395 A CA 2190595 A EP 0764332 A FI 964870 A WO 9534080 A JP 10501017 T | 02-07-1998 04-01-1996 14-12-1995 26-03-1997 23-01-1997 14-12-1995 27-01-1998 |

Form PCT/ISA/110 (patent family annex) (July 1992)

Description

Polyanilines and their Manufacture

This invention relates to polymers of the polyaniline class and to their manufacture. Polyanilines exist in at least three oxidation states (some authors recognise additional intermediate forms); the emeraldine form is particularly interesting as it is electrically conducting when suitably doped into a "salt" form (with a positive charge on the polymer backbone balanced by negative charges on adjacent ions), but the reduced leucoemeraldine form and the oxidised pernigraniline form (as well as the emeraldine form) have physical properties that may justify commercial application.

The best conventional route for synthesis of polyanilines (and substituted polyanilines) is by oxidation in an aqueous acid environment with a persulfate or other peroxy compound (for example, Abe et al, J Chem Soc, Chem Commun 1989 1728-28; Monkman et al, Synthetic Metals 40 57).

A group including A G MacDiarmid and S K Manohar (in a conference paper only briefly reported in Bull Amer Phys Soc 1982 37 p506, and in WO93/08175) has suggested that higher molecular weights can be achieved by adding a salt, such as lithium chloride, or an acid to the reaction mixture, partly to allow the reaction temperature to be reduced and partly to increase the polarity (ionic strength) of the medium, but has reported (Synthetic Metals 55-57 (1993) 977-982) that the effect on conductivity is insignificant. EP-0361429 recommends that the oxidising agent should be added dropwise to avoid the temperature rising above 5°C. Who90/0297 recommends dropwise addition of extra oxidant after the reaction has peaked, presumably to prolong the reaction time.

US5008041 proposes to oxidise a mixture of aniline and its dimer, and claims that extremely high molecular weights result. Some of these workers have used an essentially stoichiometric 1.25:1 molar ratio of oxidant to aniline; others have preferred to use an excess of aniline despite the reduced yield that this entails; in particular, Arora and Miller (Synthetic Metals 22 385-393 (1988)) have proposed that the ratio should not exceed about 1.15:1. EP-0605877 proposes to control (that is to limit) the molecular weight of the product by adding both the reagents to the reaction vessel gradually at controlled rates. Milton et al (J Phys D: App Phys 28 (1993) 1463-74) have recognised the function of N-methyl-2-pyrrolidone as a plasticiser in polyanilines.

As the paper already cited from Synthetic Metals 55-57 acknowledges, the conventional method of estimating molecular weights of polyanilines by gel permeation chromatography using polystyrenes as reference polymers gives quite inaccurate results; this is particularly so in the presence of lithium chloride as it leads to discoloration of N-methyl-2-pyrrolidone, the most practicable solvent. We have found that significantly more trustworthy estimates can be obtained by using poly-2-vinylpyridine reference polymers, and that the molecular weights of conventionally prepared polyanilines measured in this way are much lower than claimed in the literature, and in general below 50,000. (For simplicity, molecular weights quoted in this application are "mep" values, that is molecular weights corresponding to the maximum intensity in the observed peak of the gel-permeation chromatography trace; provided that peaks can be resolved, the technique permits number-average and weight-average molecular weights (M_n and M_w respectively) to be estimated, but only by integration of the trace; M_p values are considered sufficiently characterising for present purposes).

The present invention arose from a development programme (conducted in the Department of Physics of the University of Durham and in the laboratories of High Force Research) in which the inventors have found that oriented polyaniline films can be made with a much more linear structure (and significantly higher molecular weights), in consequence of which they have improved physical properties and significantly higher conductivities in the orientation direction of oriented film, and have established processes by which such polyanilines can be produced. Some of the polyanilines made in accordance with the present invention have molecular weights around 120,000 and achieve conductivities (in the orientation direction of oriented films) better than 5000 S/cm.

In accordance with one aspect of the invention, a polyaniline is characterised by a nuclear magnetic resonance spectrum in its leuco form showing only two ^{13}C peaks, indicating the substantial absence of chain branching.

Preferred polyanilines in accordance with the invention have a molecular weight (M) above 90,000 and up to about 170,000 (more especially 100,000 to 140,000).

The invention includes a preferred method of making such a polyaniline comprising oxidising aniline in aqueous solution with a persulfate and is characterised by the combination of conditions that the acidity of the solution throughout the reaction is such that if its temperature is adjusted to 30°C it will have a pH in the range from about -0.2 to +0.0; that the temperature of the solution is in the range from -4 to about -40°C; that the solution contains at least sufficient inert ionic solute to maintain it in the liquid state; and that the persulfate is added to the solution always at a rate corresponding to a total addition time of at least six hours and in a molar ratio to the aniline in the range from 1.1:1 to 1.4:1.

Preferably the addition of the persulfate does not occupy a period greater than 36 hours.

As used herein, the term "polyaniline" means a homopolymer of aniline itself, that is to say the use of polyanilines derived wholly or in part from one or more than one substituted aniline is excluded.

The acidity of the solution can be controlled by regulating the starting concentrations of the ingredients and (if necessary) the reaction time, by buffering, or by use of a drip-feed of pH adjusting additive regulated by calculation based on the expected state of reaction or on measurements of the pH of the solution (which will normally require the use of solution samples extracted and warmed to 20°C or some other temperature at which pH electrodes work reliably). If there is a sufficient concentration of chloride, it is considered sufficient to control the starting pH, as the tendency to form molecular HCl under the reaction conditions prevents the rising much above that corresponding to a pH of -0.2. Preferably the starting acidity is in the approximate range corresponding to a pH from -0.1 to 1.0. If the acidity is too great, yield of polyaniline is low, at least partly because side-reactions such as ring chlorination occur; if it is too low, polymerization fails to initiate.

Preferably the temperature is in the range between -10 and -34°C (more especially between -25 and -30°C, with an estimated optimum temperature about -25°C) throughout the reaction. Satisfactory results are obtained with the temperature held substantially constant in the specified range, but the Applicant considers it possible that there may be merit in varying the temperature in the course of the reaction (for instance slowly reducing it). If the temperature is too high, the linearity and conductivity of the polyaniline will be inadequate and its molecular weight low; if it is too low, the reaction may cease or proceed too slowly.

Very few inert ionic solutes are available, and (except when the pH is near the bottom of its permitted range and the temperature near the top of its permitted range, when hydrochloric acid may suffice) we recommend lithium chloride, magnesium chloride or sodium chloride. The oxidation reaction will not proceed if the solution freezes, and high ionic strength favours the desired long reaction times.

Slow addition of the persulfate is presumed to help increase molecular weight by favouring chain growth over chain initiation. Preferably the rate of addition is uniformly slow and preferably addition takes a period of 12 to 24 hours. Within the range specified, a higher ratio of persulfate to aniline favours high yield but a lower ratio a higher molecular weight. Ratios higher than about 1.3 appear to risk oxidation to the pernigraniline state, evidenced by purple rather than pale blue colouration in the filtrate after separation of the polyaniline. We therefore prefer to use a ratio in the range 1.15 to 1.3, with particular preferences for the range 1.2 to 1.3 or for maximum molecular weight 1.15 to 1.2. High molecular weight is usually desirable as contributing to maximum conductivity, but on the other hand may sometimes be undesirable as it reduces compatibility with other polymers, if it should be desired to use mixtures.

Preferably the film is oriented by stretching it in the presence of a substantial residue (preferably about 10-20% by weight, with the optimum at the top of the range) of solvent as plasticiser. Suitable solvent plasticisers are N-methyl-2-pyrrolidone, tetramethyl urea and 1,3-dimethyl imidazolidone (also called 1,3-dimethyl imidazolidinone). N-methyl-2-pyrrolidone (NMP) is much preferred.

The optimum degree of orientation needs to be determined by trials depending on the molecular weight and other variables; for the preferred polyanilines in accordance with the invention, this optimum corresponds to an elongation of about 800%.

The following examples illustrate the invention with reference to the accompanying drawings in which

Figure 1 represents the structures of the three principal oxidation states of polyaniline;

Figure 2, Figure 4 and each of figures 8-14 is an NMR spectrum of a different sample of leucopolyaniline in accordance with the invention;

Figure 3 an equivalent spectrum for a conventionally prepared polyaniline; and

Figure 5 is a graph of conductivity against elongation for one sample of polyaniline in accordance with the invention in oriented film form.

Figure 1 shows for reference the structural formulae of perfectly regular polyanilines in the leucoemeraldine, emeraldine and pernigraniline oxidation states respectively.

Comparison Example A

One tenth of a mole (12.96g) of aniline hydrochloride was dissolved in 150ml of distilled water and stirred in a beaker at ambient temperature (about 18°C); to this a solution of 0.125 moles (28.5g) of ammonium persulfate in 50ml of distilled water was added dropwise over a period of 4 hours, and stirring continued for a further 20 hours. The reaction mixture was then filtered and the residue washed three times with 100 ml of distilled water and stirred in 100ml of 33% aqueous ammonia for 8 hours to deprotonate the polyaniline product before neutralising and washing twice with 200ml of distilled water and once with 100ml of isopropanol. On drying under vacuum at 60°C, polyaniline with a molecular weight (M) of about 40,000 was recovered in its emeraldine p base form at a yield of about 90%.

This polyaniline was dissolved in N-methyl-2-pyrrolidone at 10% solids concentration and homogenised in a centrifuge for an hour at 4000rpm before decanting the solution to remove any fine particles. The solution was 2 coated on glass to give a coating weight of about 0.03cm and solvent partially removed by heating at 60°C under vacuum for about an hour. The coating was peeled from the glass to form a self-supporting film containing about 25% of N-methyl-2-pyrrolidone; samples around 2 by 3 cm were cut from it for orienting.

These samples were clamped at their narrow ends and the two clamps biased apart with a tension of about 5N while the temperature was raised from ambient to 80°C. This produced an elongation of about 200% and a substantial degree of uniaxial orientation. The oriented film was then protonated by exposure to 10% aqueous hydrochloric acid for 24 hours. Conductivities in the plane of the film and perpendicular to the orientation direction were measured using a standard 4-point probe and calculating by means of van der Pauw's/Montgomery's equations, and were found to be 200 S/cm and 400 S/cm respectively (compared with values around 80 S/cm for similar film in the unoriented state).

Comparison Example B

http://212.102.200.101/compdocs/000071_01-on-01-mp-040-CPDAPP-0222270308-PC-0522570021PT02-84010T0FD0

Example Temp (LiCl) Yield p
(C) (wt. %) (10,000)
- 0 0 86.6 75,000
9 -10.0 8.65 82.1 94,000
10 -15.0 11.29 82.3 117,000
11 -20.0 13.54 84.2 112,000
12 -22.5 14.89 83.8 108,000
13 -25.0 16.06 87.5 118,000
14 -25.0 16.43 84.8 120,000
15 -27.5 17.40 100.5 117,000
16 -30.0 18.09 94.9 124,000
17 -35.0 22.47 88.9 117,000

The products of Examples 9 and 16 were reduced to leucoemeraldine form for NMR measurements as before, and the resulting traces are given as Figures 6 and 7 respectively.

Examples 17-22

The procedure of Example 14 was repeated using a range of starting pH values in the range +3 to -0.3 and the results, including Example 14 to complete the sequence, are shown in Table 5 (for positive pH values, the figure shown is that of the starting solution measured at ambient temperature before cooling to the reaction temperature; for negative values, estimated by calculation from the ingredients and allowing for the relatively low degree of dissociation of HCl at this temperature and concentration).

TABLE 5

Example Starting Degree of Yield Mp

pH dissociation p 17 +3.0 1.00 89.7 117,000 18 +2.0 1.00 97.4 116,000 14 +1.0 0.85 94.8 130,000 19 0.0 0.72 94.8 127,000 20 -0.11 0.55 95.5 142,000 21 -0.23 0.58 88.9 142,000 22 -0.30 0.40 78.3 127,000

The products of Examples 17 and 22 were reduced to leucoemeraldine form for NMR measurements as before, and the resulting traces are given as Figures 8 and 9 respectively.

Examples 23-27

The procedure of Example 14 was followed, varying the amount of persulphate added over the range from 1 to 1.5 times the molar equivalent of the aniline. The yield, molecular weight and colour of filtrate were as shown in Table 6.

TABLE 6

Example Mole Yield M Colour of ratio p P filtrate 23 1.00:1 78.9 148,000 colourless 24 1.15:1 89.7 158,000 pale blue 14 1.25:1 94.8 130,000 deep blue 25 1.30:1 94.6 117,000 purple 26 1.35:1 100.3 114,000 purple 27 1.50:1 91.3 78,000 dark purple

In Table 6, the yield is expressed as a percentage of the amount of aniline present; at a molar ratio of 1.0, the yield is very close to the theoretical value of 80% for a pure 2,5-electron reaction. The coloration of the filtrate is presumably due to residual dimers (and possibly other oligomers), blue if in the emeraldine state and purple if oxidized to the pernigraniline state.

The products of Examples 23 and 27 were reduced to leucoemeraldine form for NMR measurements as before, and the resulting traces are given as Figures 10 and 11 respectively.

Example 28

This was similar to Example 20, except that the lithium chloride was replaced by 20% (27.5g) of sodium chloride and the concentration of the HCl increased to 2M (pH at room temperature -0.11). A yield of 91% (8.28g) and an M_p of 100,000 was obtained. The product of Example 28 was reduced to leucoemeraldine form for NMR measurements as before, and the resulting trace is given as Figure 12.

Examples 29-30 and Comparison Example C

The procedure of Example 14 was followed, except that the oxidant was added all at once in Comparison Example C and uniformly over different periods in Examples 29-30. In all cases the total reaction time remained at 45 hours. The results are summarised in Table 7.

TABLE 7

Example Oxidant addition Yield /Comparison time no. hours
C 0 86.5 110,000 29 7 82.9 89,000 14 14 94.8 130,000 30 36 86.3 127,000

The product of Example 29 was reduced to leucoemeraldine form for NMR measurements as before, and the resulting trace is given as Figure 13.

Comparison Example C appears to indicate that slow addition of the oxidant is not essential merely to obtain high molecular weight, but note that no NMR structure measurements are available for this sample.

Comparison Examples D-F

The procedure of Comparison Example C was repeated except that the total reaction time was varied, with the results shown in Table 8, which well illustrates that short reaction times tend to give low yields and low molecular weights.

TABLE 8

Comparison Total Reaction Yield M_p no. time (hours)
D 3 18.7 24,000
E 15 87.8 119,000
C 45 89.5 110,000
F 90 91.8 122,000

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Claims

- CLAIMS 1 A polyaniline characterised by a nuclear magnetic 13 resonance spectrum in its leuco form showing only two C peaks, indicating the substantial absence of chain branching.
- 2 A polyaniline as claimed in claim 1 having a molecular weight (M) above 50,000 and up to about 170,000.
- 3 A polyaniline as claimed in claim 2 in which the molecular weight is in the range 100,000 to 140,000.
- 4 A polyaniline substantially as described in any one of the numbered Examples.
- 5 A polyaniline as claimed in any one of claims 1-4 in oriented film form.
- 6 A polyaniline in oriented film form as claimed in claim 5 having a degree of orientation corresponding to an elongation of at least 300%.
- 7 A polyaniline in oriented film form as claimed in claim 5 having a degree of orientation corresponding to an elongation of about 300 to about 700%.
- 8 A conductive oriented film of a polyaniline as claimed in any one of claims 5-7 in its emeraldine oxidation state.
- 9 A polyaniline in oriented film form having a degree of orientation corresponding to an elongation, in the range 300 to 700% and a conductivity of at least 2000S/cm by virtue of the substantial absence of chain branching.
- 10 A method of making a polyaniline as claimed in claim 1 comprising oxidising aniline in aqueous solution with a persulphate and characterised by the combination of conditions that the acidity of the solution throughout the reaction is such that if its temperature is adjusted to 20°C it will have a pH in the range from about -0.2 to +3.0 that the temperature of the solution is in the range from -5 to about -40°C; that the solution contains at least sufficient inert ionic solute to maintain it in the liquid state; and that the persulphate is added to the solution always at a rate corresponding to a total addition time of at least six hours and in a molar ratio to the aniline in the range from 1.1:1 to 1.4:1.
- 11 A method as claimed in Claim 7 in which the starting acidity corresponds to a pH in the range -0.1 to +1.0.
- 12 A method as claimed in Claim 10 or Claim 11 in which the temperature is in the range -10 to -34°C.
- 13 A method as claimed in Claim 10 or Claim 11 in which the temperature is in the range -25 to -30 C.
- 14 A method as claimed in Claim 10 or Claim 11 in which the temperature is about -20 C.
- 15 A method as claimed in any one of claims 10-14 in which the said inert ionic solute is selected from the group consisting of lithium chloride, magnesium chloride, and sodium chloride.
- 16 A method as claimed in any one of claims 10-15 in which addition of the said persulfate is uniform over a period of at least 12 hours.
- 17 A method as claimed in any one of claims 10-16 in which the addition of the persulfate occupies a time not greater than 36 hours.
- 18 A method as claimed in any one of claims 10-17 in which the ratio of persulfate to aniline is in the range from 1.16 to 1.3.
- 19 A method as claimed in any one of claims 10-18 in which the ratio of persulfate to aniline is in the range from 1.2 to 1.3.
- 20 A method as claimed in any one of claims 10-19 in which the ratio of persulfate to aniline is in the range from 1.15 to 1.2.
- 21 A method of making a polyaniline substantially as described with reference to any one of Examples 1-27.
- 22 A method of making a polyaniline substantially as described with reference to Example 28.
- 23 A method of making a polyaniline substantially as described with reference to Example 29 or Example 30.
- 24 Polyaniline made by the method claimed in any one of claims 10-23.
- 25 Polyaniline as claimed in claim 24 in the form of oriented film.

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Fig.1.

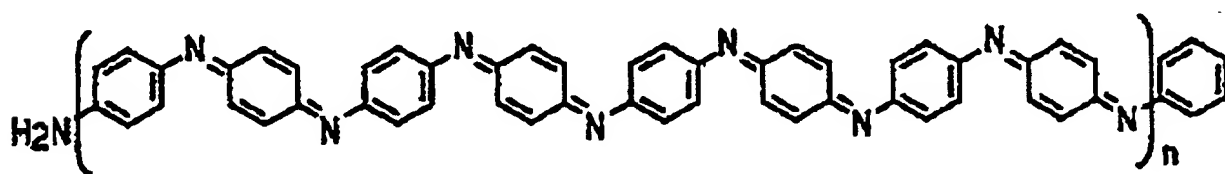
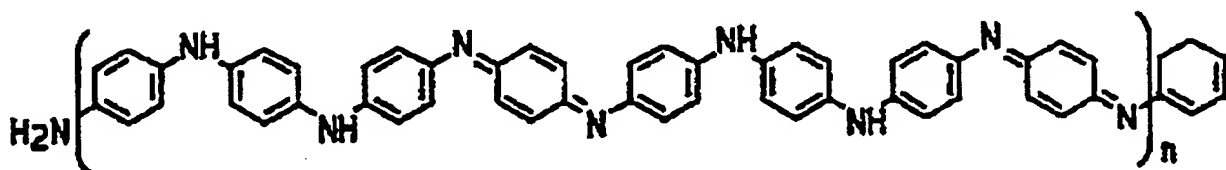
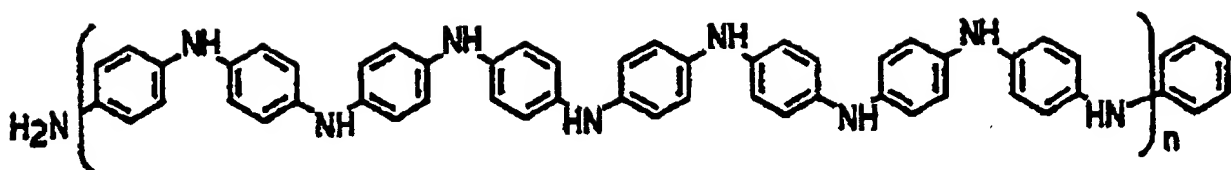
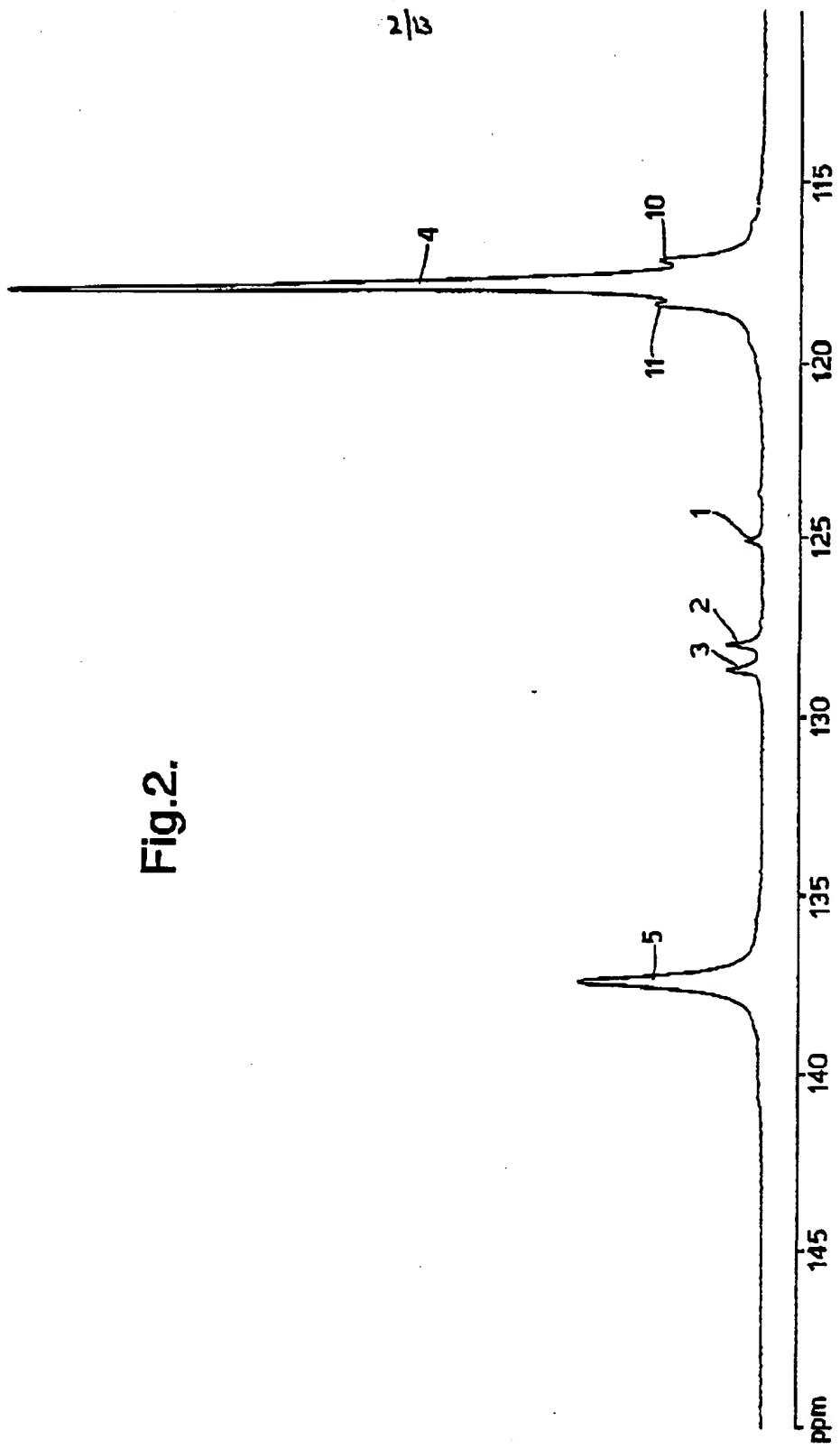


Fig.2.



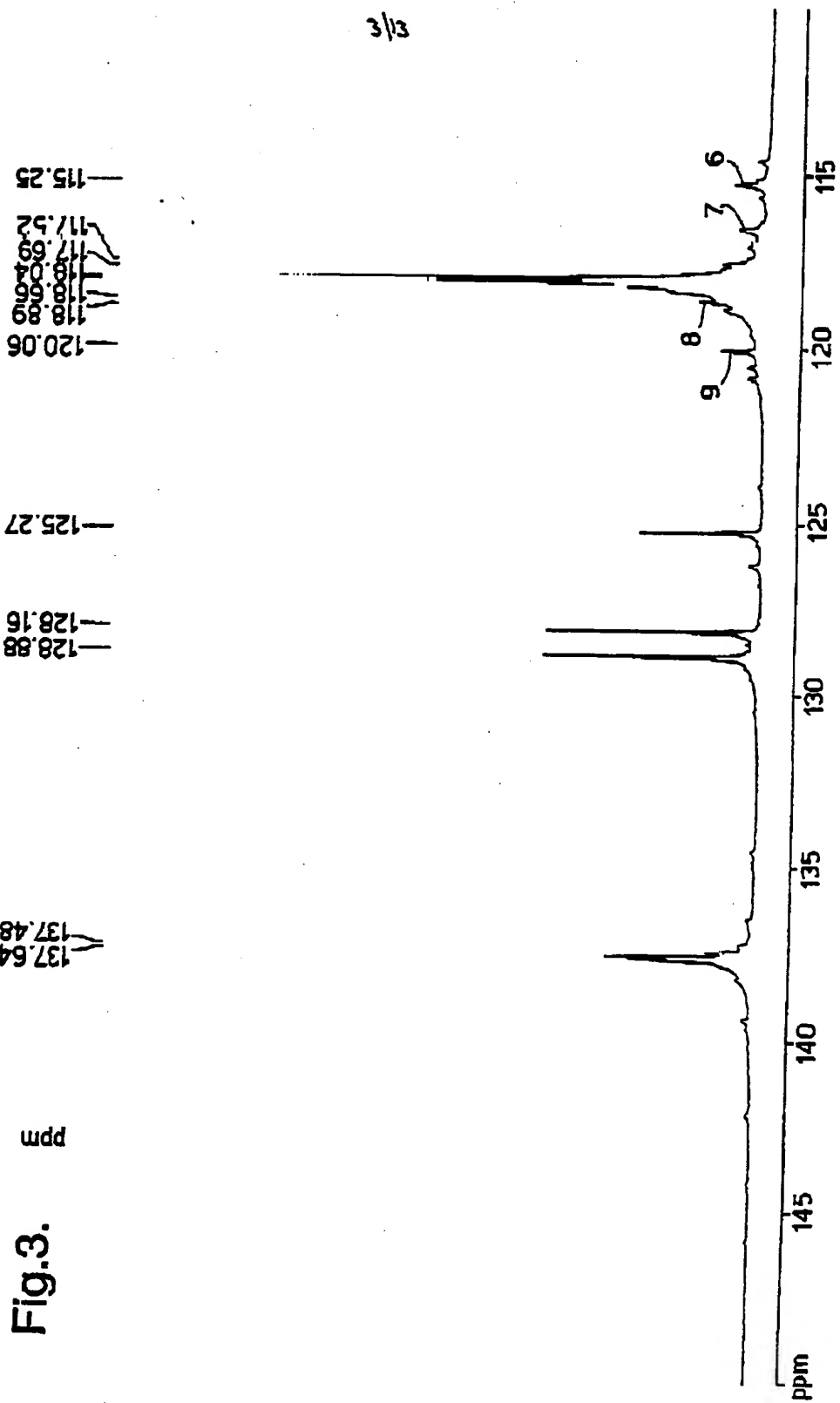


Fig.3.

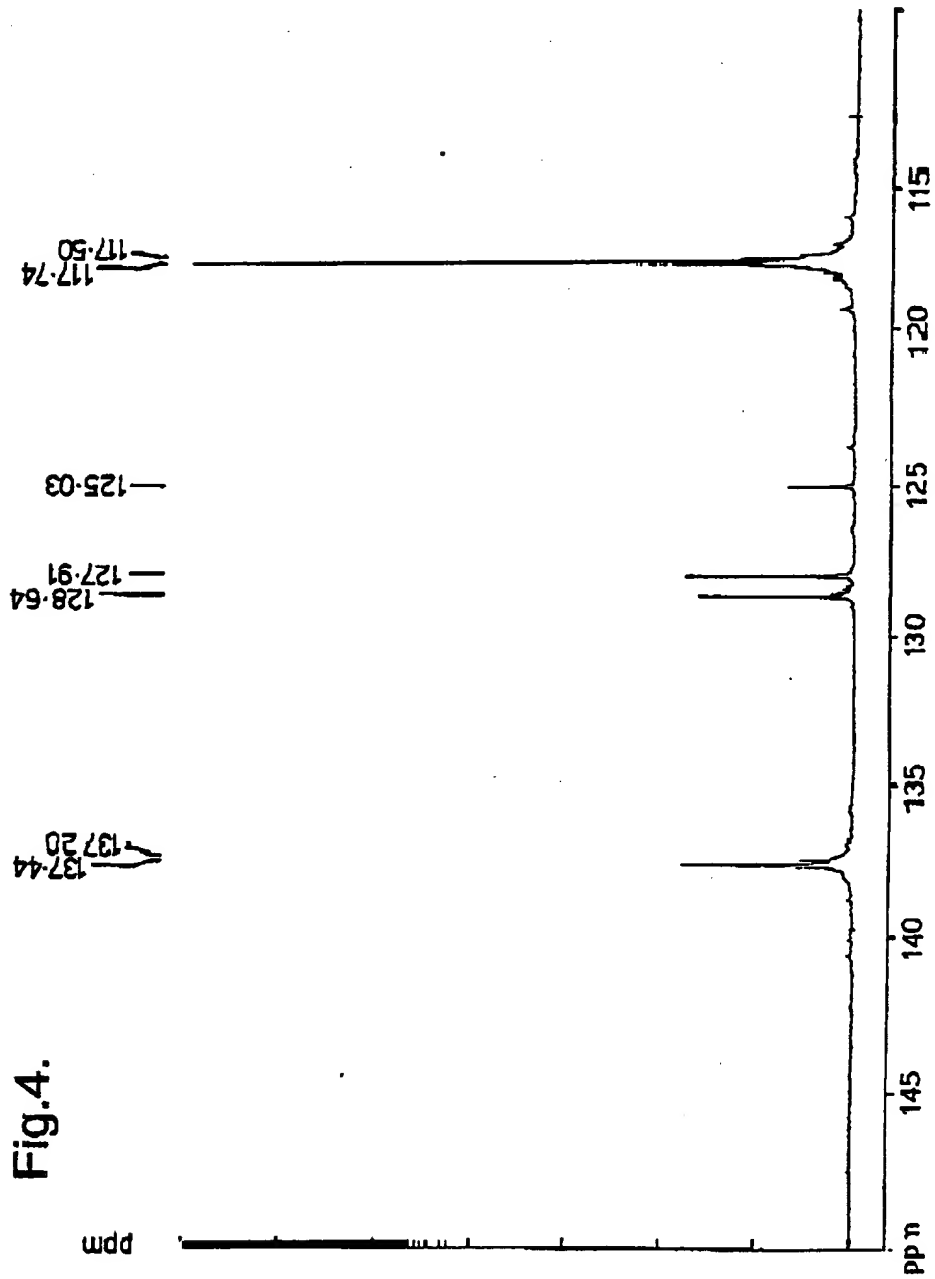
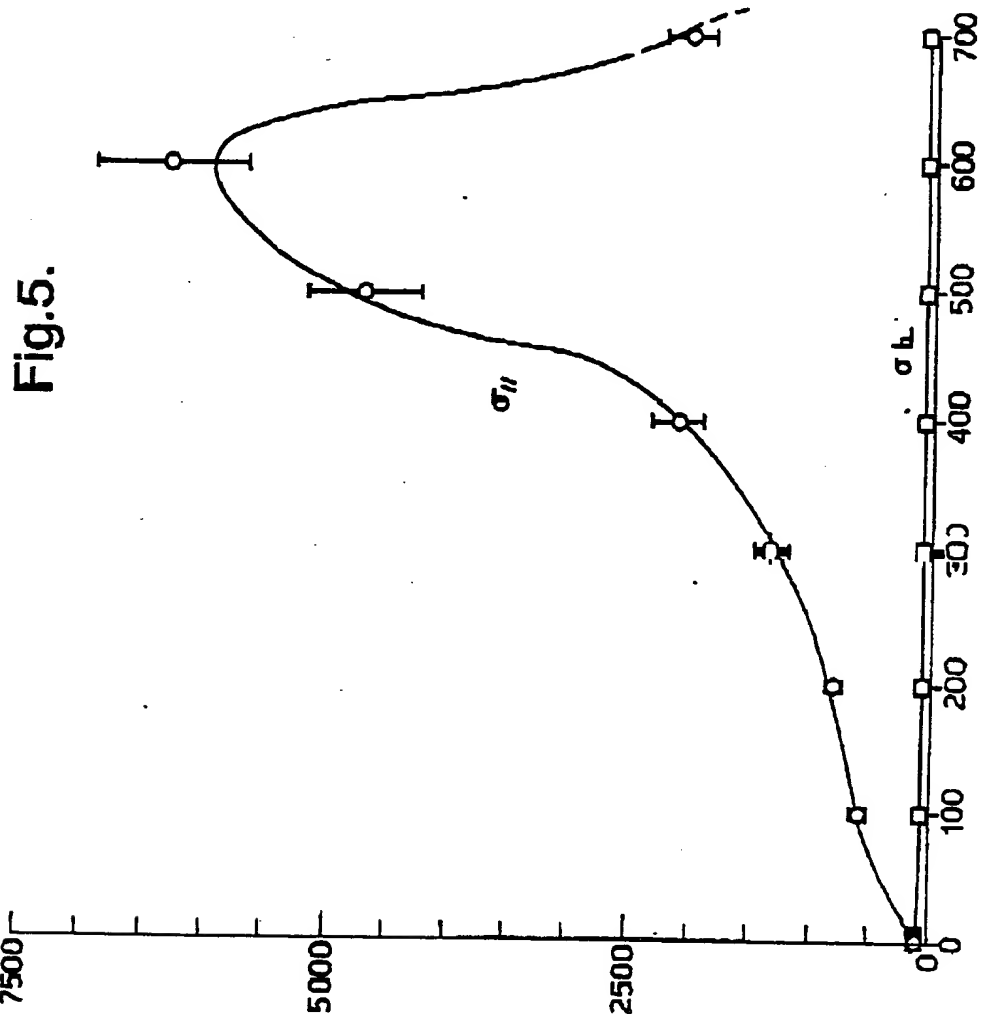


Fig.4.

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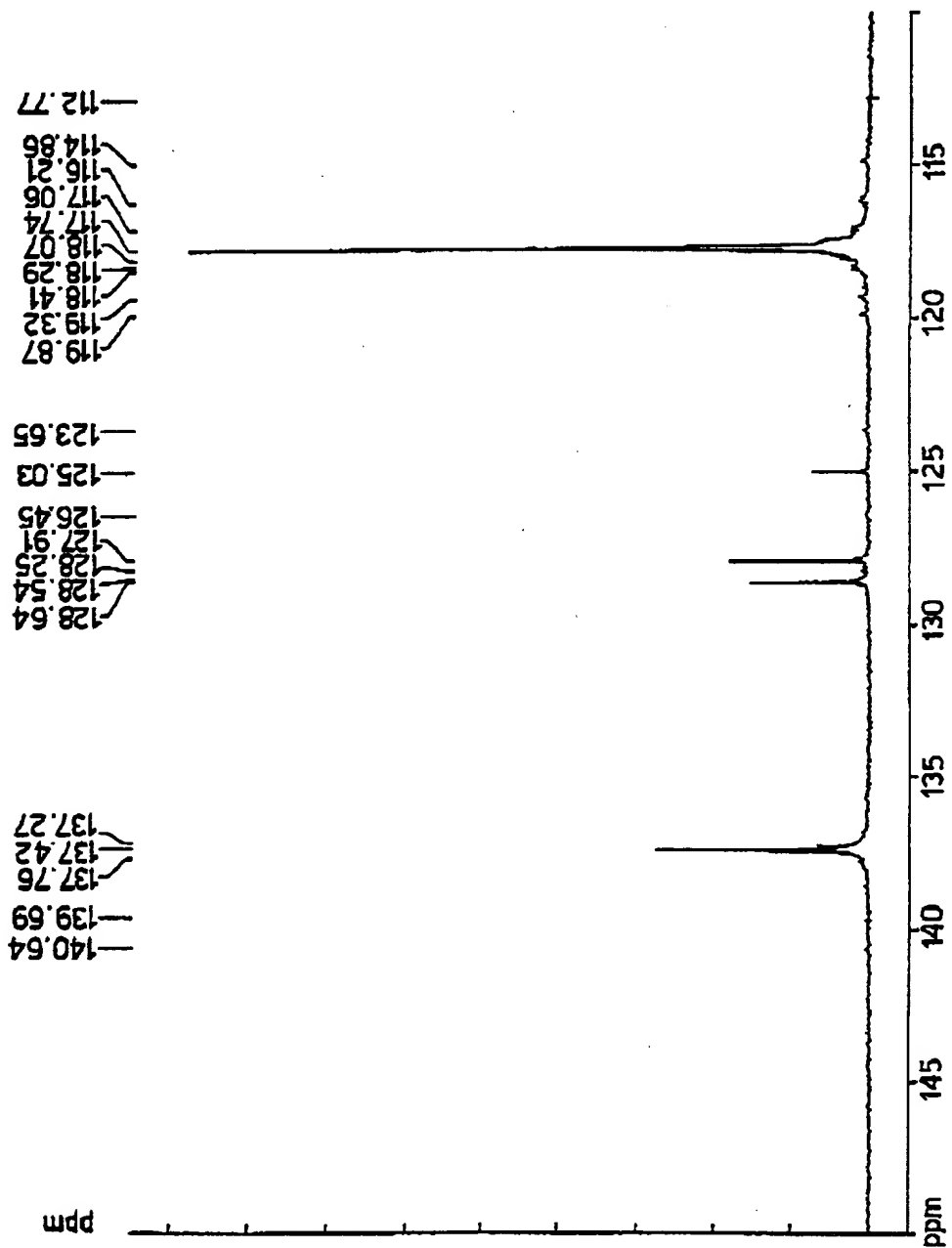


Fig. 6.

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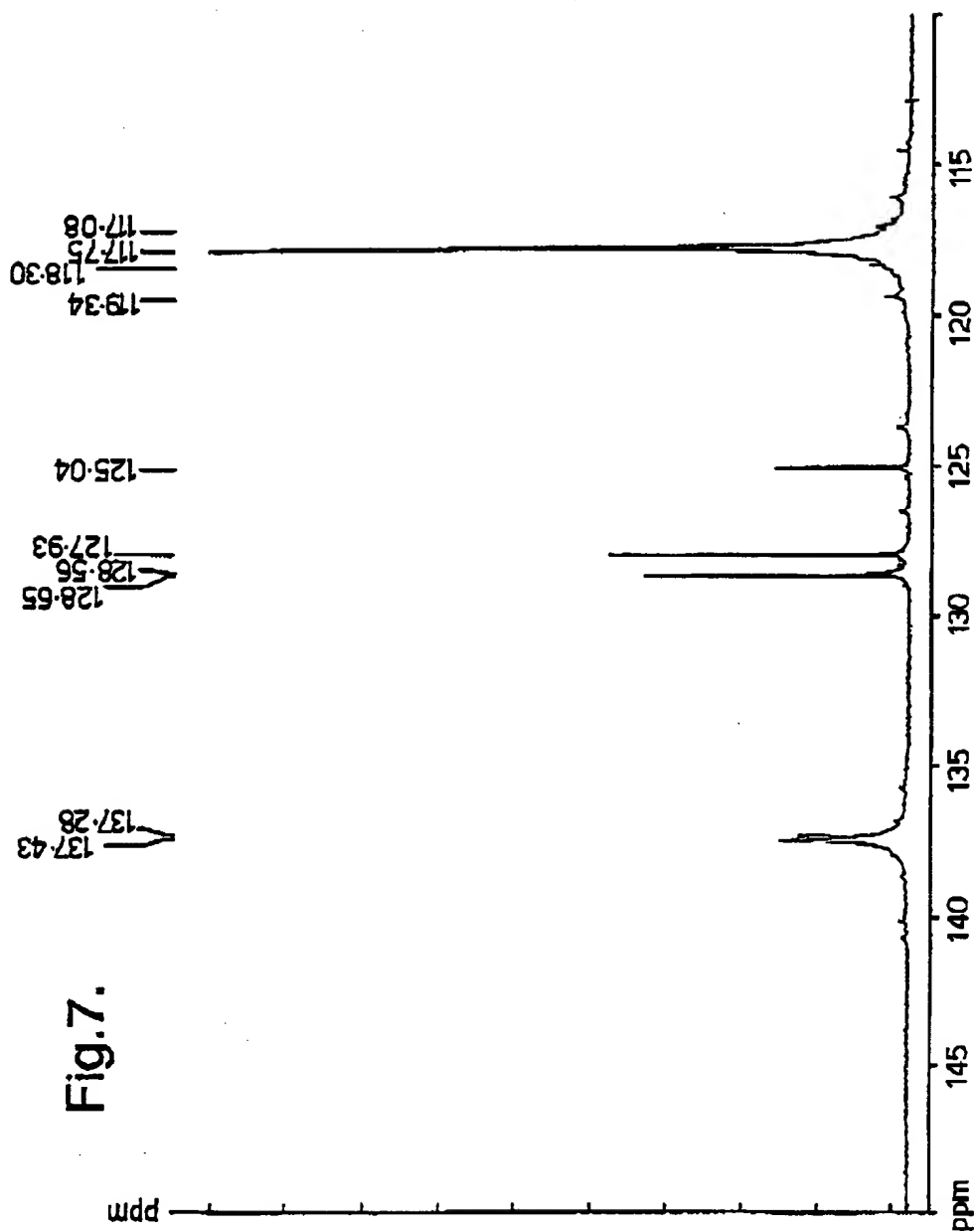
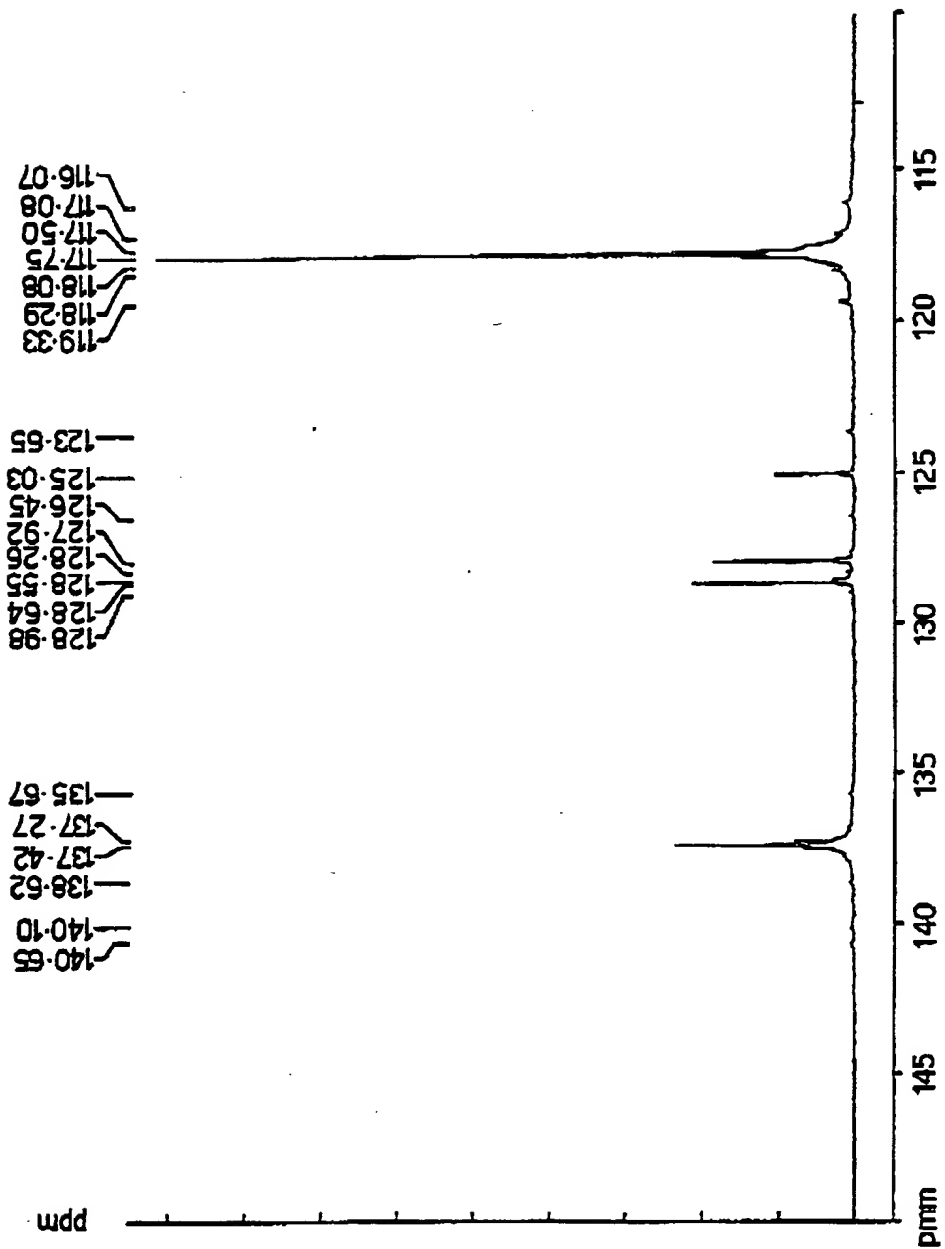


Fig.7.

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Fig. 8.



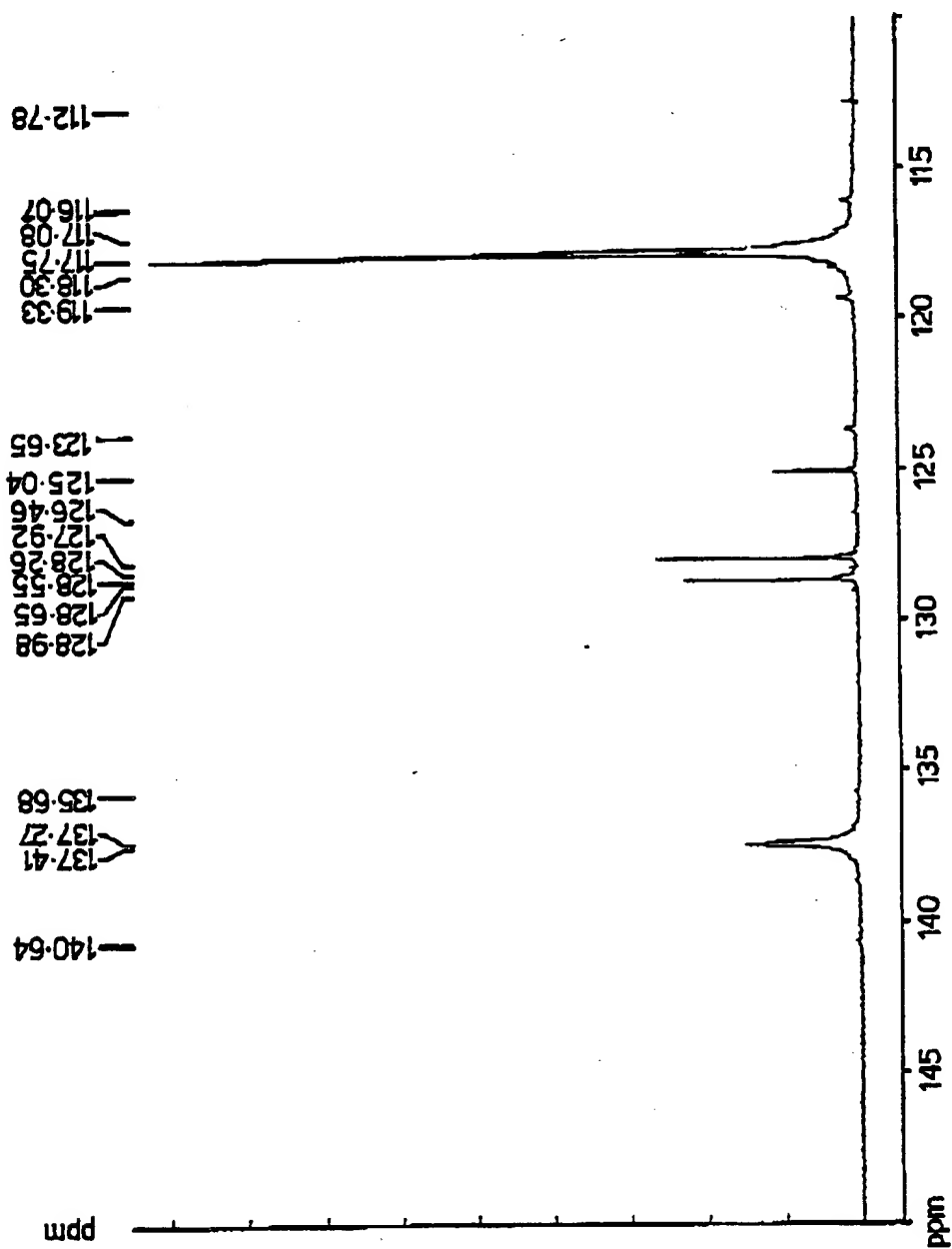
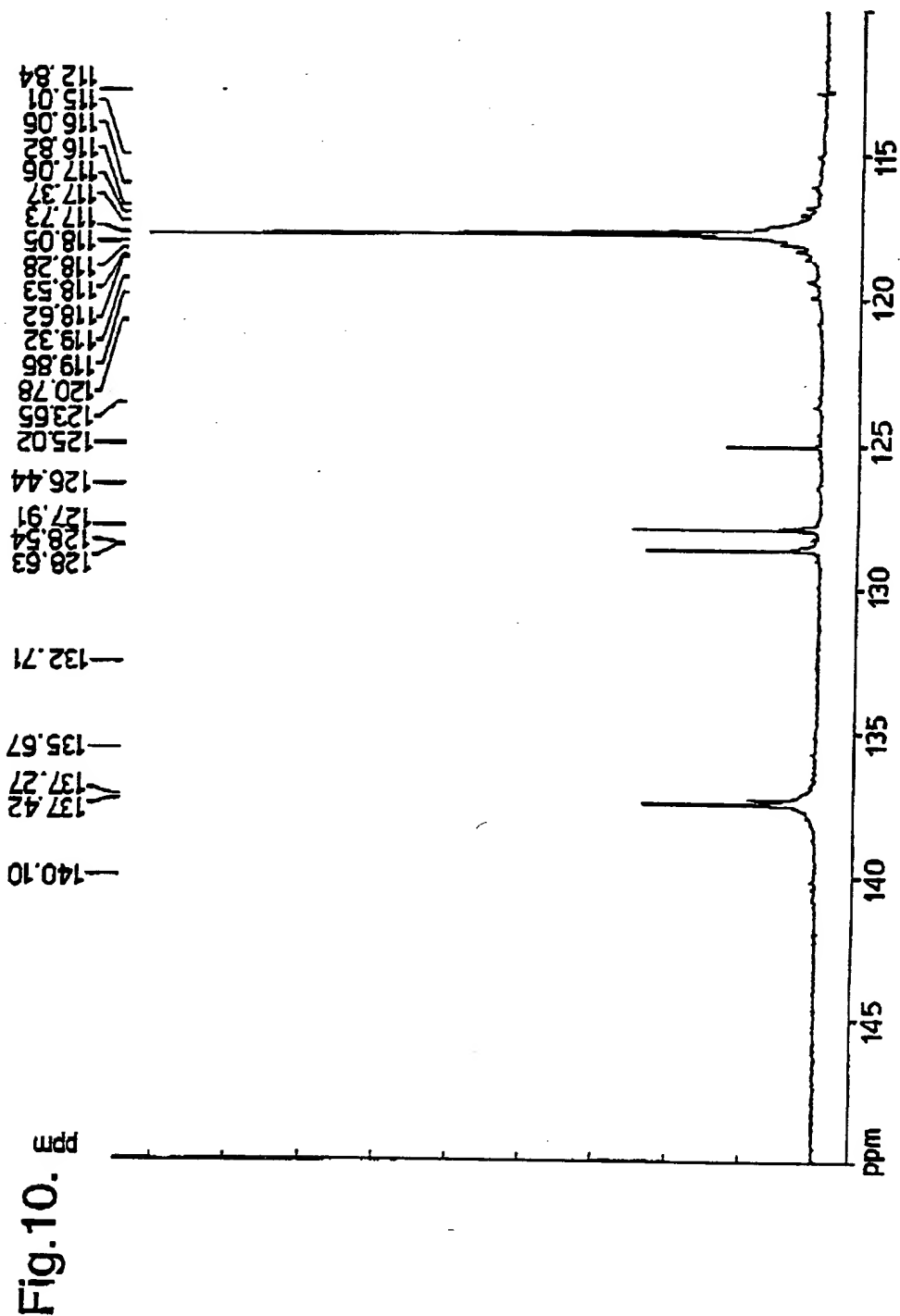


Fig.9.



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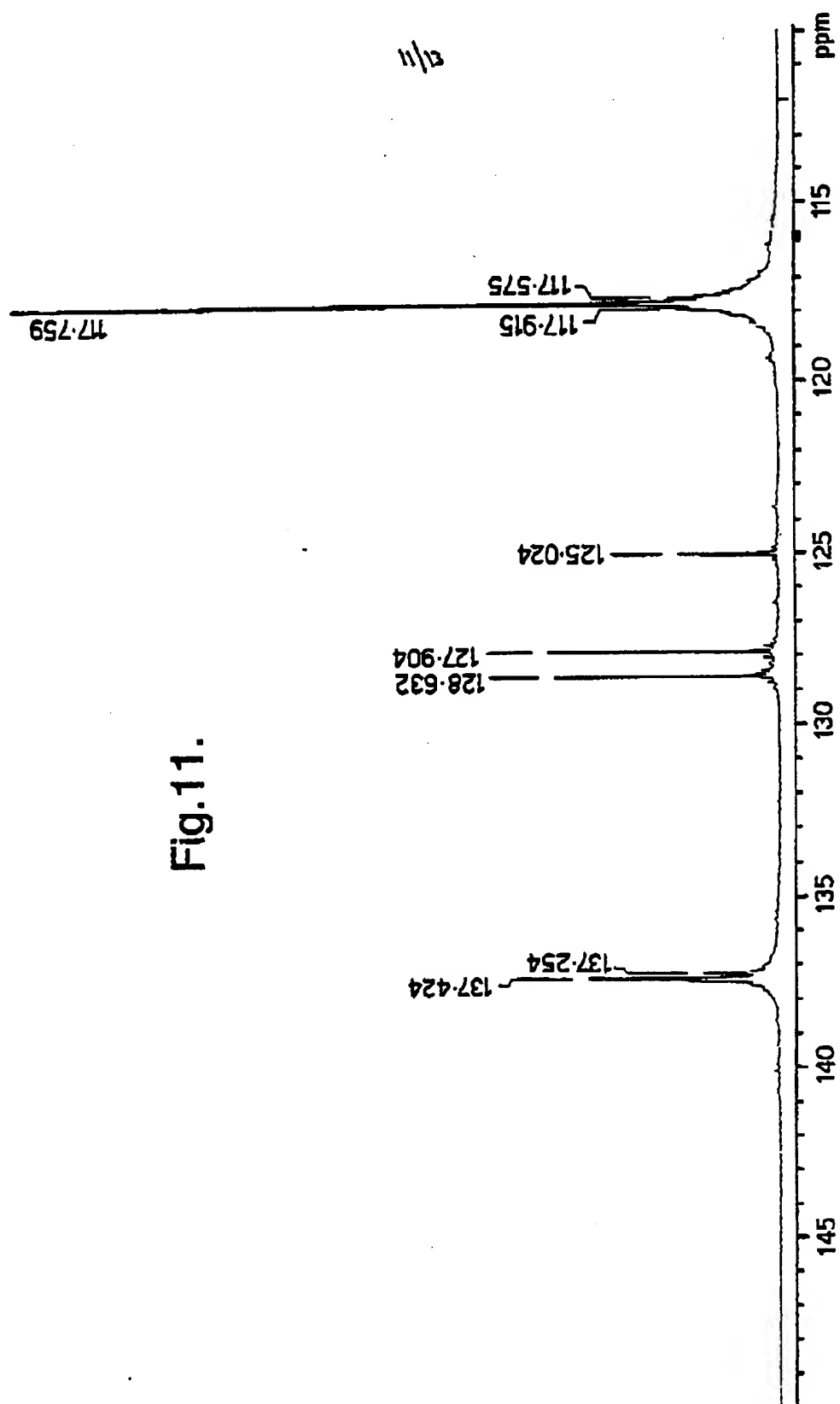


Fig.11.

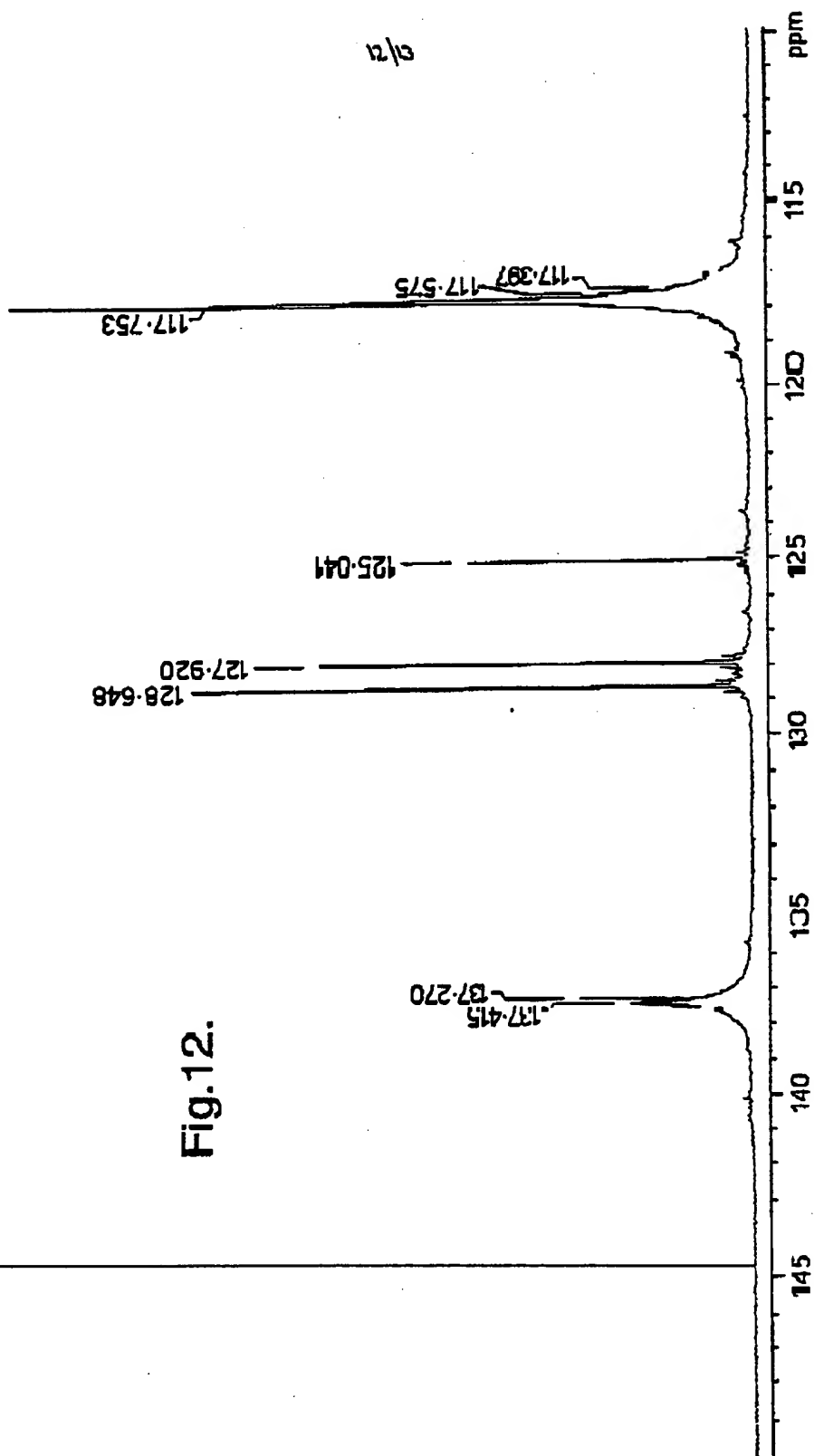


Fig.12.

